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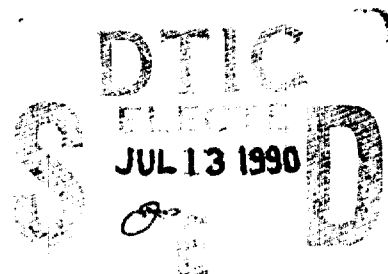
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STABILITY OF LIQUID PROPELLANTS UNDER LONG-TERM STORAGE

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19. **ABSTRACT** (cont)

Analyses were conducted on the gas and liquid phase before and after exposure to determine the effect of temperature and impurities on the composition, to identify and quantify degradation products, and to predict the decomposition mechanism.

These data and techniques will be used to determine container design for long-term storage of the propellant, to provide analytical methodology for monitoring the LP 1846 during production and storage, to determine the effects on LP 1846 during long-term storage, and to relate propellant composition and condition with the results from ballistics testing.

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INTRODUCTION

The U.S. Army has been engaged in the search for insensitive munitions for guns in tanks and self-propelled howitzers. Preliminary vulnerability tests indicated that liquid propellants, stored in one-gallon metal and plastic containers, were insensitive to ignition when impacted by a shaped charge and secondary hot fragments (ref 1). This feature and logistical, ballistic, and cost savings advantages prompted an extensive program to characterize liquid propellants. The study produced information that liquid propellants were sensitive to degradation when exposed to transition metals and other non-metallic substances (ref 2). The knowledge of the decomposition rate of the basic liquid propellants constituents when exposed to contaminants and the aging effects from a long-term storage is essential. Any significant deviation in the basic propellant formulation will result in a loss in ballistic performance.

At the present time, there are no fail-safe criteria established for liquid propellants under long-term storage conditions. A methodology has been developed that will establish the stability of liquid propellants in storage. To facilitate the acquisition of data, accelerating temperature testing was employed. The rate data generated can be useful for determining the design of storage containers. Ultimately, a fail-safe manual will be prepared that will outline the acceptance testing for liquid propellants exposed to long-term storage conditions.

BACKGROUND

The two most prominent liquid gun propellants, LP 1845 and LP 1846, were selected for the Fail-Safe Criteria Program evaluation. The typical composition for each liquid propellant is given in table one.

Table 1. Liquid propellant formulations

| | <u>Percentages (%)</u> | |
|-----------------------------------|------------------------|----------------|
| | <u>LP 1845</u> | <u>LP 1846</u> |
| Hydroxylammonium nitrate (HAN) | 63 | 61 |
| Triethanolammonium nitrate (TEAN) | 20 | 19 |
| Water | 17 | 20 |

Low level concentration of impurities such as ammonium nitrate (AN), ethanolammonium nitrate (EAN), diethanolammonium nitrate (DEAN), nitric acid, nitrosoamines, and trace amounts of transition metal (TM) ions can be expected to be found.

The program requires analytical techniques to monitor liquid propellant compositions in the gas and liquid phase during long-term storage, and these had to be devised. A stability apparatus for accelerated pressure-time studies over a temperature range of 25°C to 65°C was designed. The accelerated test data will be used to establish the safety criteria for the long-term storage of liquid propellants as a function of temperature and contaminants. The analytical results will be coordinated with ballistic and accelerating rate calorimetry (ARC) data.

The necessity to characterize the effects of contaminants on liquid propellants prompted the design of experiments which would illustrate their role. Fe^{+3} and Cu^{+2} were selected as the transition metal contaminants for exposure to the liquid propellant. In addition, various concentrations of nitric acid were evaluated for its effect upon liquid propellant stability at various temperatures. The temperature range selected for this study was 25°C to 65°C. Pressure-time data were recorded for neat and contaminant spiked propellant at selected intervals. Analyses were conducted before exposure for comparison at the conclusion of each experiment. For these data, the kinetics and mechanism of decomposition will be determined as well as the establishment of liquid propellant specifications and pressure build-up during long-term storage.

PROCEDURE

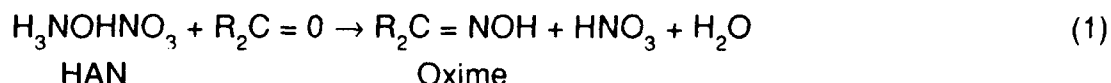
An intensive review of analytical methodology for liquid propellants was conducted. Techniques were selected and tested for applicability. An assessment of these techniques is given in table 1. The analytical techniques selected for monitoring the fail-safe criteria are listed in table 2. The LP 1846 underwent a pretest screening program to determine the extent of pressure buildup and effect of contaminants. This information will be used to establish the container design necessary for long-term storage. Individual samples of each liquid propellant will be placed in a controlled temperature environment of 25°C, 50°C, and 65°C for long-term storage. At intervals of 3, 6, and 12 months, a sample will be extracted and completely characterized. At each of these time intervals, a ballistic performance test will be determined for each sample. A comparison of these data will be made with the ballistic data for unexposed liquid propellant fired in the same weapon.

ANALYSIS FOR WATER

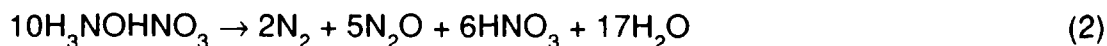
The analytical method selected for the water analysis was the Karl Fisher titration method (ref 3). Hydranal Composite 2 or 5 was used as the titrant. Hydranal Composite 2 provided greater precision and titrant stability. Methanol with 10% acetic acid was used as the solvent. For each analysis, the sample size was contingent upon the type of titrant used.

**ANALYSES FOR HYDROXYLAMMONIUM NITRATE (HAN),
TRIETHANOLAMMONIUM NITRATE (TEAN),
ETHANOLAMMONIUM NITRATES (EAN & DEAN),
AND AMMONIUM NITRATE (AN)**

The titrimetric method developed by Dr. Kasler at the University of Maryland was reviewed as a potential technique for HAN/TEAN analysis (refs 3 and 4). Kasler used methyl isobutyl ketone to convert HAN to an acidic product for titration. Since the oxime is a very weak acid ($K_b < 10^{-12}$), it is not titrated, and the actual titration is based on the nitric acid liberated during the formation of oxime.



In samples with significant decomposition, this is a serious problem since nitric acid is a product of decomposition (proposed, ref 5) (eq 2).



The actual stoichiometry of the LP decomposition proposed in equation 2 will be established by gas and liquid phase analyses of the LP during storage. Therefore, an analytical method was required to differentiate free nitric acid from the nitric acid produced from the ketone/HAN reaction. This was made possible by eliminating the ketone, allowing the HAN to remain unchanged, and titrating the free nitric acid which was present. The effect of titration without ketone in which the HAN and TEAN form one peak separate from the free nitric acid peak is shown in figure 1.

Acetone was found to provide better titration curves with sharper end-points and less noise than titration with the methyl isobutyl ketone prescribed by Dr. Kasler. It was found that the base used as a titrant was important since tetrabutyl ammonium hydroxide (TBAH) produced sharper end-points than did the n-butyl amine (NBA) (fig. 2). Large samples were used with pre-addition of titrant to produce quicker, more accurate results. The presence of impurities such as AN, ethanolammonium nitrate (EAN), and diethanolammonium nitrate (DEAN) has a large effect on the TEAN determination. The effect of impurities on the TEAN peak is illustrated in figure 3. It is obvious from this figure that the value of TEAN can be suspect due to the lack of sufficient separation from AN, EAN, and DEAN.

Therefore, for HAN, TEAN, EAN, DEAN, and AN, ion chromatography (IC) was the method of choice selected for quantification and qualification of these compounds. An IC-Pak TM column and a conductivity detector were used for the separation and detection. A 100 μ l size sample of liquid propellant (diluted to 1/5000 in water) was injected using 4 mm HNO_3 /5% methanol as the eluent. The separation using this technique is shown in figure 4 (ref 6).

Potentiometric titration was chosen as the reference method for checking the concentrations of major components detected by IC analysis. Since the HAN can be detected very accurately by titration, it would be used as a key factor in the confirmation of results between the two methods. For TEAN, the other ethanolammonium nitrates, and AN, the titration would be used as a visual, semiquantitative correlation check. TBAH (0.2 N) in methanol was used as the titrant. The solvent for this method was 50 ml of ethanol/acetone (100:1). A 0.6-gram sample size with a pre-addition of 15.0 ml titrant was used for the analysis.

ANALYSIS FOR NITRIC ACID

The formation of nitric acid as a product of decomposition (eq 2) poses a serious problem in the stability of liquid propellant and for this reason must be accurately monitored.

An analytical method was required to differentiate free nitric acid from the nitric acid produced from the ketone/HAN reaction. This was achieved by eliminating the ketone to allow the HAN to remain unchanged and then titrating the free nitric acid which was present. As depicted in figure 1, HAN and TEAN form one peak separate from the free nitric acid peak when titrated without the ketone.

A potentiometric titration was selected for the nitric acid determination. The titrant used was 0.01 N TBAH in methanol with 50 ml of ethanol as the solvent. For concentrations of HNO_3 less than 0.5%, a 1-gram sample was chosen, and for concentration of HNO_3 greater than 0.5%, a 0.5-gram sample is required.

ANALYSIS OF METALS

The analysis of metals can be adequately determined by several techniques such as inductively coupled plasma (ICP), atomic absorption (AA) polarography, and ion chromatography (IC). The unavailability of ICP and AA instrumentation led to the investigation of polarography and IC.

Polarography was used to develop methods for Cu^{+2} , Ni^{+2} , Fe^{+3} , and Cr^{+6} (table 3). The ability of the liquid propellant to act as oxidizer, reducing agent, or chelating agent for species of the transition metals (TM) complicated the polarographic analyses. This

fact was made evident when ICP data were compared to polarographic data for iron (table 4)¹. The difference between the two illustrates that most of the Fe^{+3} in the liquid propellant is in a complexed state and not available for polarographic detection as Fe^{+3} . As a result, IC was investigated and feasibility studies conducted on metal spiked samples of liquid propellant. Preliminary data indicate that IC will provide both quantitative data for all species of interest as well as oxidation states. This information will be useful in determining the role of metal impurities in liquid propellants.

The preliminary investigations led to the selection of ion chromatography for metals analysis. A μ Bond pak C18 column with a 2mMNaOS/50mM tartaric acid (pH adjusted to 3.4 with 50% NaOH) eluent at a flow rate of 1.0 ml/min was used. The post column reactant (PAR) flow rate was 0.5 ml/min. An ultraviolet (UV) detector at 520 nm was required for the identification of the metals present. The samples were diluted 1/10 in water, and the injection volume was 100 μ l. The IC chromatogram is shown in figure 5².

ANALYSIS FOR OTHER CONTAMINANTS

The presence of nitrosoamine, nitramine, and morpholine contaminants in the liquid phase will be determined by liquid chromatography. The contaminants found in the gas phase will be detected, quantified, and qualified by gas chromatography. These contaminants will consist mainly of NO_x species. Mass spectrometry will be used as the reference for both analyses.

PRESSURE-TIME STUDIES

Besides the need for analytical methods to monitor the LP during storage, it is essential to establish the extent of pressure build-up in the storage containers. A stability apparatus was designed (fig. 6) to maintain the liquid propellant in an inert helium atmosphere. Pressure measurements were recorded at selected time intervals as a function of temperature and concentrations of known contaminants.

¹ Research contribution by M. Decker, BRL, 1988.

² Research contribution by J. Krol, Waters Division of Milipore, 1988.

PHYSICAL PROPERTY STUDIES

Vapor pressure (LP-2) (fig. 7) and density (LP-3) (fig. 8) measurements were also determined for LP 1846 for use in pressure-time study calculations.

The vapor pressure was measured as a function of temperature in an apparatus similar to the pressure-time study apparatus in figure 6. The sample was degassed and sealed under vacuum in the ampoule. The changes in mercury levels were made with a cathetometer. For the density measurements, the degassed sample was sealed in a calibrated glass picnometer. The changes in the liquid level were measured with a cathetometer as a function of temperature.

KI TEST

To establish the relative sensitivity of the liquid propellants, a standard test used for solid propellants, the KI Test, was conducted. This test was conducted to provide safety guidelines by comparison with a solid propellant prior to storage in long-term storage chambers. The KI test of LP 1846 was compared to nitroguanidine, a typical solid explosive, and found to be very insensitive. Nitroguanidine reacts in 10 to 20 minutes, and the LP 1846 did not react in over 140 minutes at 82.5°C.

LONG-TERM STORAGE STUDIES

Samples will be placed in long-term storage chambers at 25°C, 50°C, and 65°C. For each set of conditions a large sample will be prepared for ballistics and a small sample for analyses. Samples will be pulled from inventories under each set of conditions after 3, 6, and 12 months for the ballistics testing and compositional analyses.

DISCUSSION AND RESULTS

The data from the analytical and pressure-time studies provided information for predicting pressure build-up during long-term storage, speculation as to the decomposition process, factors involved in the rate of liquid propellant degradation, and insight into the complex chemistry of the liquid propellants.

The rate data from the pressure-time studies was extrapolated to predict the pressure build-up during long-term storage. For neat propellant and propellant contaminated with iron, copper, and nitric acid, the extrapolated pressure build-up after one year of storage is shown in table 5 as a function of temperature and ullage. In most of the cases, the pressure build-up is too excessive for either glass or plastic containers and will require adjustment of the vapor space to permit long-term storage testing.

Both lots of LP 1846 (LP-2: Lot #ABY87FS2C013 and LP-3: Lot #1846-01) were analyzed to determine their composition prior to testing in these studies. The compositional analysis of LP 1846 (table 6) appears to be consistent with equation 2 for the decomposition of HAN. All of the species presently being monitored are given in table 6. Other species such as AN, ethanolammonium nitrates (EAN and DEAN), nitrosamine and gas phase decomposition products are currently under investigation and will be presented in future reports. The formation of nitric acid is linear with respect to temperature and concentrations of contaminants (table 7). Further confirmation and clarification will be available when testing is completed on a current production lot of liquid propellant.

The pressure-time curves for LP 1846 show very distinct patterns for each of the contaminants tested which are very consistent regardless of the temperature (figs. 9 through 12).

When nitric acid is present at 0.5 to 1.0%, a very rapid initial rate is observed which levels off in 10 to 20 days.

The presence of iron causes an erratic initial rate, followed by a slow acceleration. This is followed by a short period at which the rate remains constant and finally a second acceleration which also equilibrates after a short time interval. The erratic rate is probably due to the inaccessibility of the iron due to complexation. The second acceleration is a result of the build-up of nitric acid which causes more of the iron to exist in the Fe^{+3} state through oxidation of the Fe^{+2} and less of the complexed iron due to the lower pH. The final rate is a function of both the iron and the nitric acid.

The copper on the other hand produces a very rapid initial rate similar to that observed for nitric acid. Apparently the copper is not tied up as is the iron, permitting it to cause immediate rapid decomposition. This is followed by de-acceleration and then equilibrium at a constant rate. In this case, the copper appears to initiate rapid decomposition. As it is converted from the +2 to the +1 state, the rate is slowed due to lesser accessibility of Cu^{+2} , since there is no available mechanism for oxidation to the +2 state. During the de-acceleration, the nitric acid begins to take over as the rate governing specie. The final rate occurs when all of the copper has been converted to the +1 state, and the nitric acid takes over.

The presence of these contaminants is very detrimental to the stability of liquid propellants. Of the three, nitric acid appears to have the greatest effect since it is a product of decomposition of all contaminants. It also causes decomposition in three ways (1) by itself through a mechanism which has not been clarified, (2) by oxidation of Fe^{+2} to Fe^{+3} which catalyzes decomposition, and (3) by lowering the pH and thereby

lowering the concentration of the free amines which tie-up transition metals by complexation. The elimination of the presence and potential for formation of nitric acid through the absence of transition metals and neat nitric acid in the production lots will enhance the stability of liquid propellants.

CONCLUSIONS

Analytical methodology has been selected for monitoring the liquid propellants during storage.

1. Techniques have been chosen which provide adequate sensitivity, selectivity, accuracy, and precision.

2. The Karl Fisher water titration is simple, straight-forward, and provides acceptable results.

3. Ion chromatography of HAN, TEAN, EAN, DEAN, AN, and the transition metals will provide a rapid, precise method for these components.

4. The state of the metals present is probably very complex as observed by the results for iron by polarography. For this reason, inductively coupled plasma was chosen as confirmation method for the transition metals.

5. The potentiometric titrations which will be used as confirmation for HAN, TEAN, and nitric acid were enhanced by

- a. Use of acetone to provide sharp, noise-free peaks (HAN & TEAN)

- b. Derivative titration mode to enhance the end-point

- c. Pre-addition of titrant to provide a fast titration with the necessary precision (HAN & TEAN)

- d. Differentiation of the source of the nitric acid. Ketone-free solvent was used for free nitric acid (nitric acid).

The pressure-time studies have provided insight for the complex chemistry of liquid propellants.

1. The pressure build-up during long-term storage of liquid propellants has been calculated.

Storage containers for these tests have been selected.

2. Patterns of rates of decomposition caused by various contaminants have been observed.

a. Nitric acid causes accelerated decomposition rates.

b. Iron catalyzes decomposition which accelerates after formation of nitric acid. The acceleration is due to the oxidation of Fe^{+2} to $^{+3}$ as well as the additive effect of the presence of nitric acid.

c. Copper causes rapid initial decomposition, followed by de-acceleration due to conversion of Cu^{+2} to $^{+1}$. Finally, the rate continues due to presence of the nitric acid which was formed.

3. The ability to detect small changes in nitric acid concentration makes it a good indicator of propellant stability and condition. The potential for the use of nitric acid as a flag is under consideration.

4. The current studies indicate the need for data from contaminant free liquid propellant to confirm present conclusions.

RECOMMENDATIONS

The current data illustrates the need to evaluate contaminant free production lots to determine their stability as a function of temperature. The data will be used for comparison to contaminated lots to clarify the effect of each contaminant. It is important to finish the characterization of the effects of contaminants currently being studied and to explore the effects of other materials which will contact the liquid propellant during some phase of its use. Also, the continuation of the characterization of both the gas and liquid phases before and after exposure to elevated temperatures and contaminants is essential to establish decomposition mechanisms and kinetics equations. The effectiveness of inhibitors on the stability of uncontaminated and transition metal spiked liquid propellant will be evaluated to provide a means, if necessary, for stabilization. The correlation of these data will result in the ability to accurately predict the effect of long-term storage of liquid propellants, establish their useful lifetime, establish specifications, provide a means for monitoring their condition and effectiveness as well as to establish safety criteria in their handling.

Table 2. Analytical monitoring techniques

| <u>Component</u> | <u>Confirmation</u> | <u>Recommended</u> |
|-----------------------------------|---|--|
| HAN | Titration | IC-sensitive to small variations |
| TEAN | Titration - does not resolve from other weak acid impurities (AN, etc.) | IC-sensitive to small variations |
| H ₂ O | Titration | Titration |
| Nitric acid | Titration | Titration |
| Metals | ICP-polarography too complex and time consuming | IC-all TM ⁺² one run; TM ⁺³ method being developed |
| AN, EAN, DEAN | Titration | IC |
| Gas phase degradation products | MS | GC-two column method |
| Liquid phase degradation products | MS | LC-being developed |

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Table 3. Polarographic methods for LP 1846

| <u>Electrolyte</u> | <u>Ratio</u> | <u>Additive</u> | <u>pH</u> | <u>Potential, V</u> | <u>Matrix</u> | <u>Sensitivity, NA/ppm^a</u> | | | |
|---|--------------|-----------------|-----------|---------------------|--------------------|--|------------------------|------------------------|------------------------|
| | | | | | | <u>Cu⁺²</u> | <u>Ni⁺²</u> | <u>Fe⁺³</u> | <u>Cr⁺⁶</u> |
| 1NKSCN/LP | 9/1 | 5T | | -0.53 -0.9 | LP | 18 | 15 | | |
| 2MK ₂ CO ₃ /LP | 5/5 | 7.6T | 6 | -0.90 | LP | | | 100 | |
| 1NKSCN/s.Na OH/c.HNO ₃ ^b | 7/1.6/1 | 5T ^c | 1 | -0.47 -0.78 | Ashed ^d | 20 | 58 | | |
| s.Malonic/ c.HNO ₃ ^b | 7/1 | 5T ^c | <2 | -0.06 | Ashed ^d | | | 856 | |
| 1NNaOH/s.Na OH/c.HNO ₃ ^b | 7/1.6/1 | | >10 | -0.75 | Ashed ^d | | | | 14 |

^d Ashing samples are in 1 ml concentrated HNO₃

^c Additive 5T is 0.005% triton

^b s. denotes saturated; c. denotes concentrated

^a NA/ppm denotes nanoamps/ppm

Table 4. Metals analysis of LP 1846 (LP-2 and LP-3)

| <u>Metal</u> | <u>LP-2, ppm</u> | <u>LP-3, ppm</u> |
|--------------|------------------|---|
| Iron | <0.09 | 2.06 (polarography: 0.31 ppm Fe ⁺³) |
| Chromium | 0.74 | 0.40 |
| Copper | <0.18 | <0.17 |
| Nickel | 0.88 | 0.34 |
| Cobalt | <0.09 | <0.09 |
| Lead | <0.87 | <0.87 |
| Tin | 3.06 | 3.03 |

Note: The ICP metals analysis data were obtained through the efforts of BRL (ref 7). The difference between polarography and ICP illustrates that the Fe⁺³ in the LP is complexed and not available as Fe⁺³.

Table 5. Pressure build-up in liquid propellant storage containers

| LP 1846 Type | Temp, °C | Pressure, psig/yr at ullage: | | | |
|------------------------|----------|------------------------------|-----|-----|---------|
| | | 25% | 50% | 75% | 50%/3yr |
| 0.44% HNO ₃ | 25 | 1.7 | 0.8 | 0.6 | 2.6 |
| 0.44% HNO ₃ | 50 | 38 | 20 | 13 | 58 |
| 0.44% HNO ₃ | 65 | 186 | 93 | 62 | 278 |
| 0.54% HNO ₃ | 65 | 134 | 67 | 45 | 200 |
| 0.98% HNO ₃ | 65 | 280 | 140 | 94 | 420 |
| 2ppm Fe | 25 | 0 | 0 | 0 | 0 |
| 2ppm Fe | 50 | 0 | 0 | 0 | 0 |
| 2ppm Fe | 65 | 64* | 32* | 21* | 96* |
| 7ppm Fe | 25 | 0 | 0 | 0 | 0 |
| 7ppm Fe | 50 | 7.6 | 3.8 | 2.5 | 11.4 |
| 7ppm Fe | 65 | 238 | 119 | 79 | 357 |
| 25ppm Fe | 50 | 112 | 56 | 38 | 168 |
| 25ppm Cu | 50 | 57 | 28 | 19 | 86 |
| 50ppm Fe | 25 | 0.2 | 0.1 | 0.1 | 0.3 |
| 50ppm Cu | 25 | 0.2 | 0.1 | 0.1 | 0.3 |
| 50ppm Fe | 50 | 190 | 95 | 64 | 284 |
| 50ppm Cu | 50 | 105 | 52 | 35 | 158 |

* Denotes current rates from pressure-time studies that are still in progress.

Table 6. Compositional analysis of LP 1846 before and after exposure and rate of decomposition as a function of temperature and contaminants at 65% ullage

| <u>LP 1846</u> | <u>Temp, °C</u> | <u>%HAN</u> | <u>%TEAN</u> | <u>%Water</u> | <u>%HNO₃</u> | <u>Days</u> | <u>Rate</u> |
|------------------------|-----------------|-------------|--------------|---------------|-------------------------|-------------|------------------|
| LP-2 ^a | | 59.3 | 19.3 | 19.7 | 0.44 | | |
| 0.44% HNO ₃ | 25 | 59.7 | 19.9 | 20.0 | 0.48 | 136 | 0.1 |
| 0.44% HNO ₃ | 50 | 58.4 | 20.4 | 20.5 | 0.74 | 116 | 2.0 |
| 0.44% HNO ₃ | 65 | 57.7 | 20.1 | 20.3 | 1.18 | 48 | 8.5 |
| LP-3 ^a | | 59.4 | 20.3 | 19.5 | 0.03 | | |
| 2.1ppm Fe | 25 | 60.0 | 20.6 | 19.2 | 0.12 | 120 | 0 |
| 7.25ppm Fe | 25 | 59.9 | 20.4 | 20.1 | 0.14 | 120 | 0 |
| 51.0ppm Fe | 25 | | | | | 107 | <0.01 |
| 49.4ppm Cu | 25 | | | | | 107 | <0.01 |
| 2.1ppm Fe | 50 | 59.8 | 20.5 | 19.5 | 0.23 | 120 | 0 |
| 7.0ppm Fe | 50 | 59.5 | 20.7 | 19.6 | 0.28 | 120 | 0.42 |
| 23.8ppm Fe | 50 | | | | | 63 | 4.2 ^b |
| 24.5ppm Cu | 50 | | | | | 63 | 2.8 ^b |
| 49.9ppm Fe | 50 | 58.4 | 21.6 | 19.4 | 0.80 | 70 | 9.0 |
| 49.2 | 50 | 57.5 | 20.3 | 20.2 | 1.03 | 84 | 5.0 |
| 2.1ppm Fe | 65 | | | | | 40 | 3.0 ^b |
| 2.1ppm Fe | 65 | | | | | 40 | 6.6 ^b |
| 0.54% HNO ₃ | | | | | | | |
| 2.1ppm Fe | 65 | | | | | 30 | 13.4 |
| 0.98% HNO ₃ | | | | | | | |
| 6,9ppm Fe | 65 | | | | | 40 | 8.0 ^b |

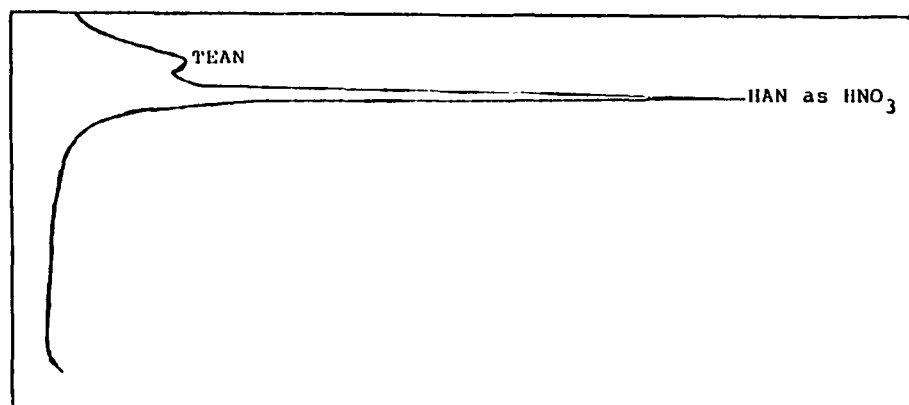
^b All rates are final rates in mmHg/day. These are still in progress.

^a Initial composition (LP-2: Lot # ABY87FS2C013) (LP-3: Lot # 1846-01).

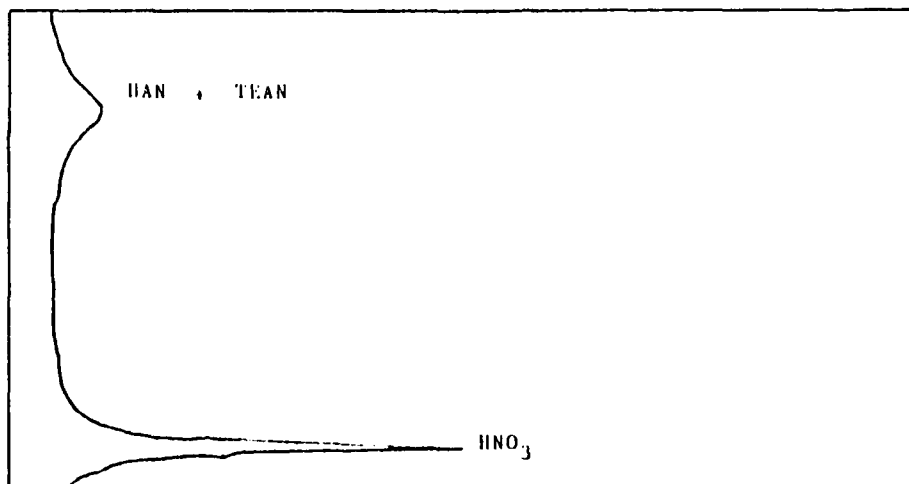
Table 7. Loss of HAN and formation of nitric acid for LP 1846
as a function of temperature

| <u>Temp, °C</u> | <u>HAN loss</u> <u>(ug/g/day)</u> | <u>HNO₃ formation</u> <u>(ug/g/day)</u> | <u>Initial %:</u> | | | |
|-----------------|--------------------------------------|---|-------------------|------------------------|-----------|-----------|
| | | | <u>HAN</u> | <u>HNO₃</u> | <u>Fe</u> | <u>Cu</u> |
| 25 | 6.62* | 2.94 | 59.3 | 0.44 | 0.0 | 0.0 |
| 25 | 15.8* | 7.5 | 59.4 | 0.03 | 2.1 | 0.0 |
| 25 | 19.2* | 9.2 | 59.4 | 0.03 | 7.2 | 0.0 |
| 50 | 75.0 | 25.9 | 59.3 | 0.44 | 0.0 | 0.0 |
| 50 | 35.0* | 16.7 | 59.4 | 0.03 | 2.1 | 0.0 |
| 50 | 44.2* | 20.8 | 59.4 | 0.03 | 7.0 | 0.0 |
| 50 | 135.7 | 110.0 | 59.4 | 0.03 | 50.0 | 0.0 |
| 50 | 223.8 | 119.0 | 59.4 | 0.03 | 2.1 | 50.0 |
| 65 | 344.7 | 157.4 | 59.3 | 0.44 | 0.0 | 0.0 |

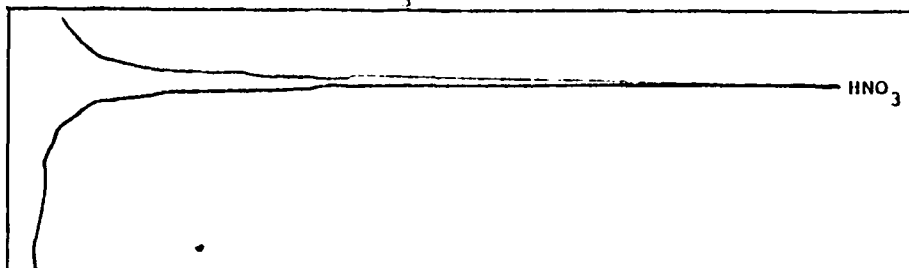
* Calculation based on formation of nitric acid and proposed ratio of 10:6 for HAN:nitric acid from equation 2.



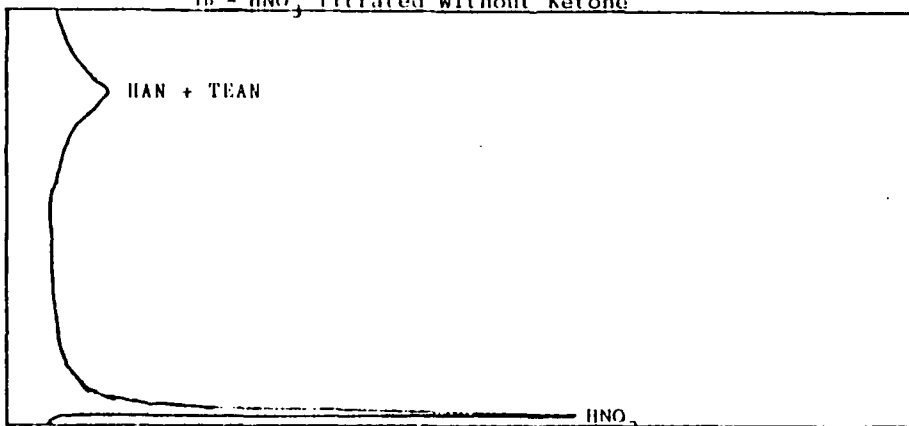
1d - LP Titrated With Ketone



1c - LP Plus HNO_3 Titrated Without Ketone

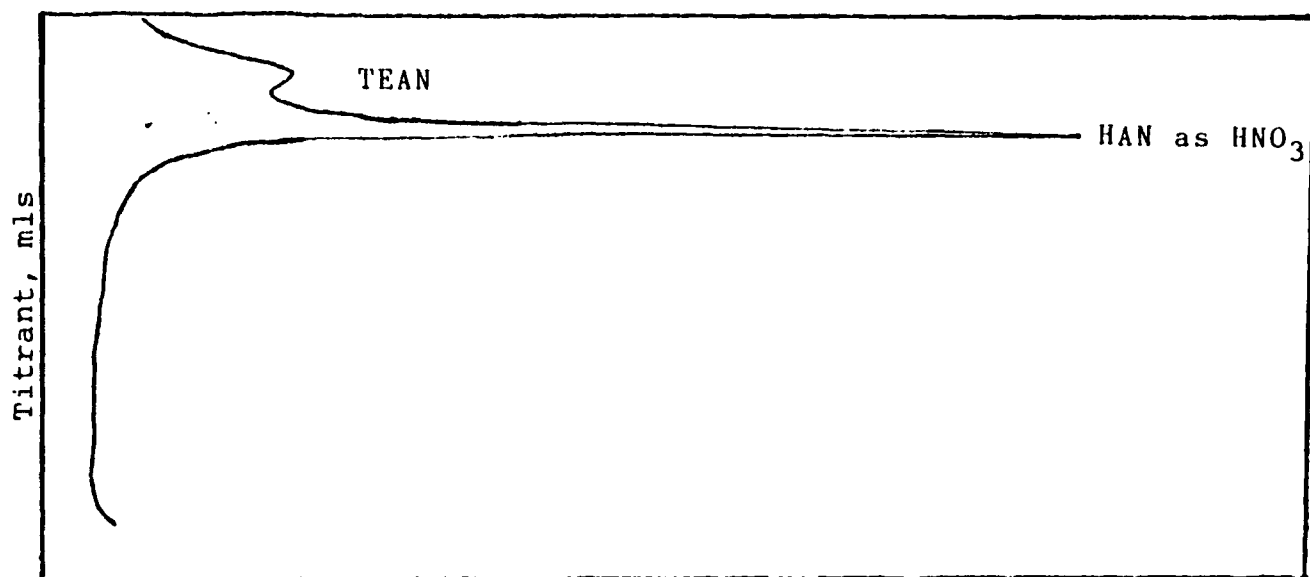


1b - HNO_3 Titrated Without Ketone

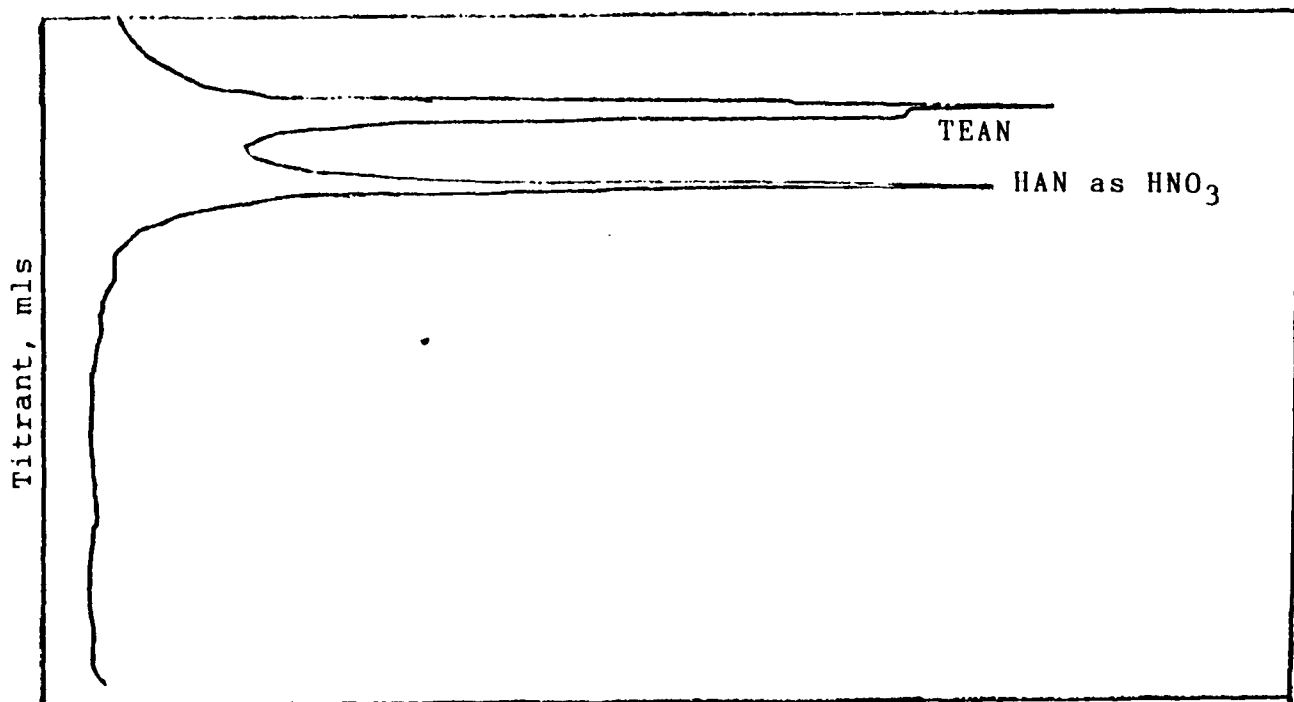


1a - LP Titrated Without Ketone

Figure 1. Effect of ketone in solvent on titration of acid

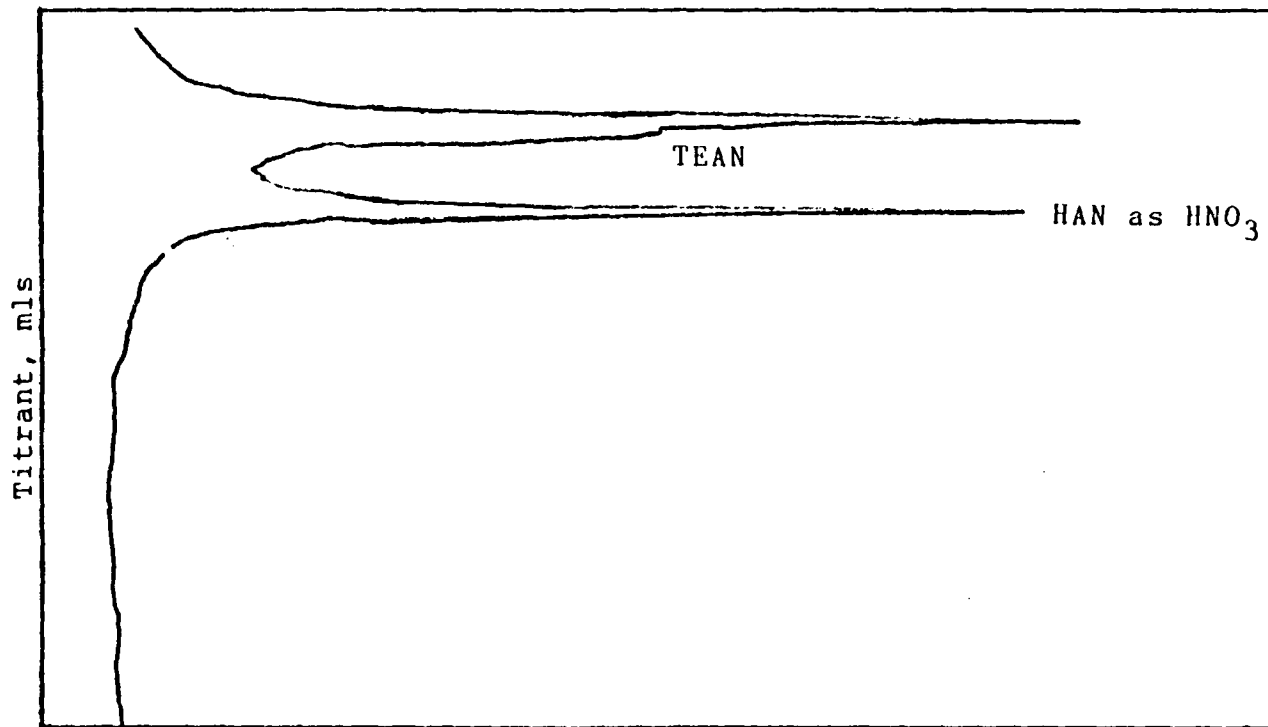


2b - n-Butylamine Titrant

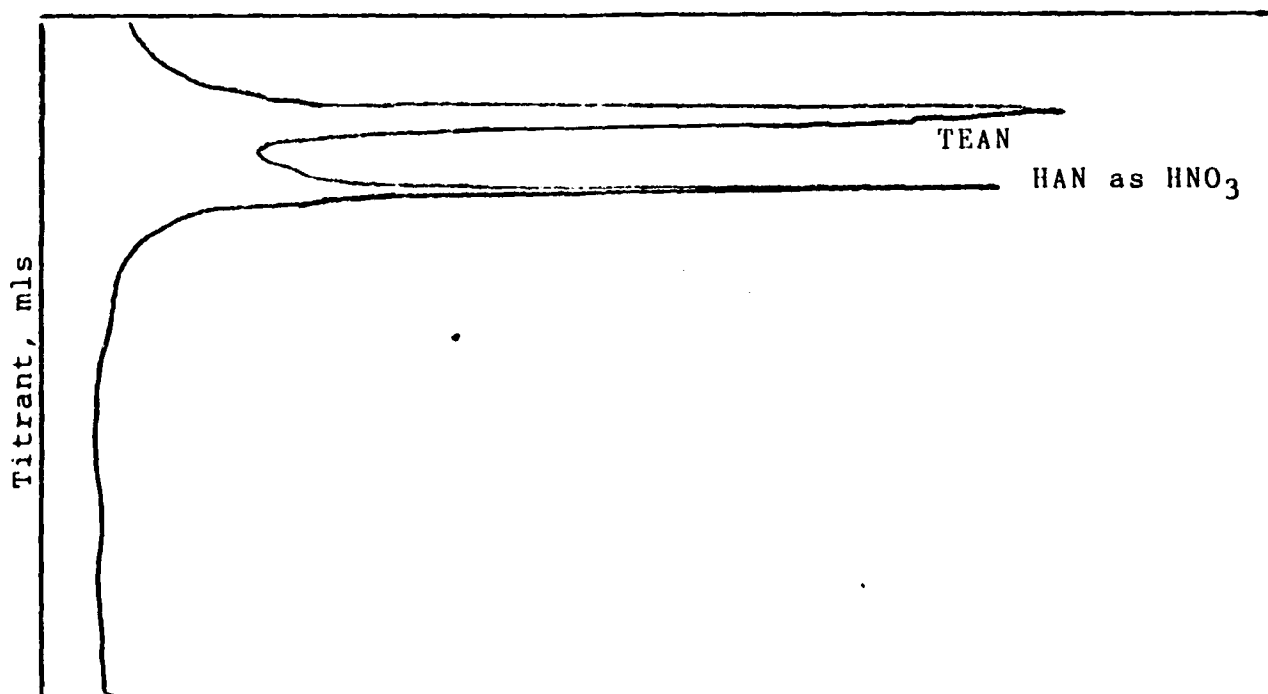


2a - Tetrabutyl Ammonium Hydroxide Titrant

Figure 2. Comparison of derivative curves for liquid propellant using both titrants



3b - LP + Ammonium Nitrate



3a - LP Only

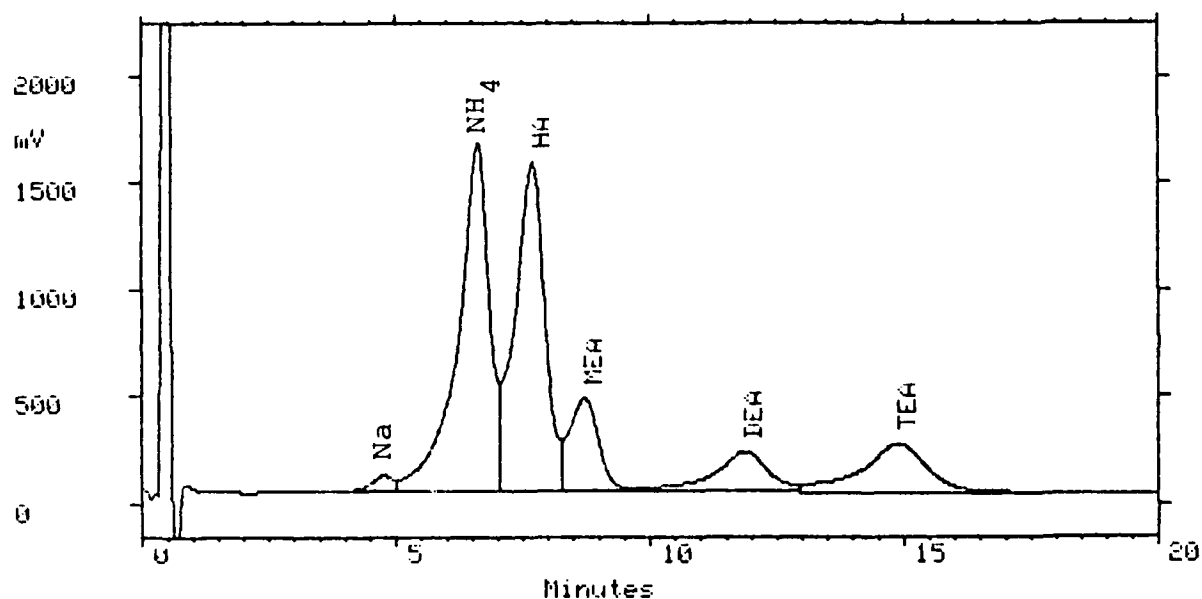
Figure 3. Comparison of liquid propellant titration curves for impurities

Ethanolamine Analysis

IC-Pak TM; 4mM HNO3 / 5% MeOH at 2 ml/min; BP=2000psi

Conductivity Detection; BC=1230uS

Chromatogram of EANH4

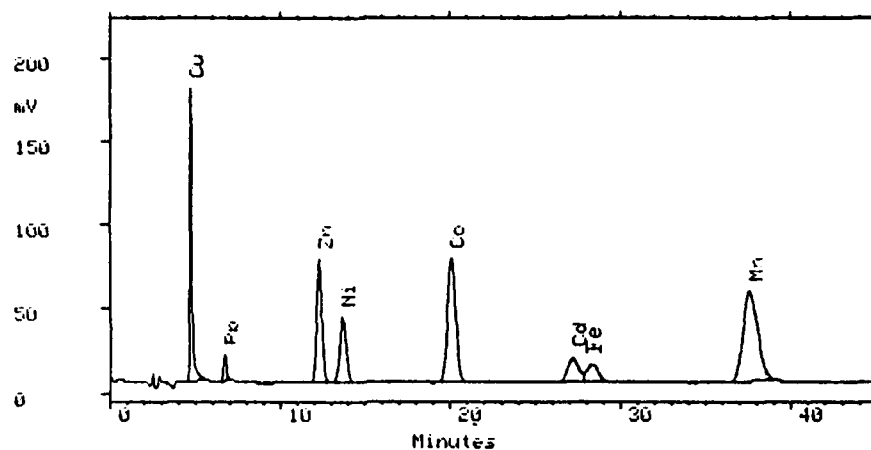


| Peak Name | Ret time | Area | Height | Type | Amount |
|-----------|----------|----------|---------|------|--------|
| UNKNOWN | 3.92 | 276688 | 10490 | BV | 0.000 |
| UNKNOWN | 4.77 | 2385708 | 80525 | VV | 0.000 |
| UNKNOWN | 6.62 | 71343328 | 1645115 | VV | 0.000 |
| HA | 7.70 | 63314572 | 1545812 | VV | 48.643 |
| MEA | 8.72 | 17685564 | 434004 | VV | 22.739 |
| DEA | 11.88 | 14440178 | 185728 | VV | 22.386 |
| TEA | 14.90 | 20399112 | 224761 | VB | 54.090 |

Figure 4. Chromatogram of cation standards

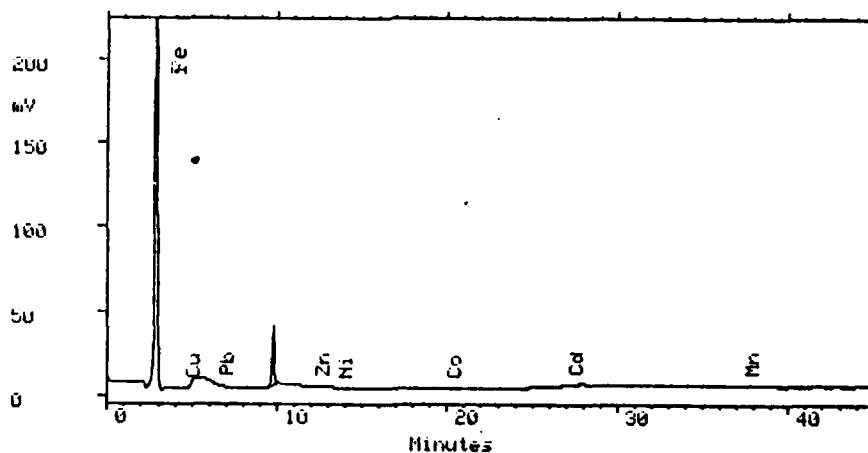
Transition Metal Method; uBondapak C18
 2mM NaDS / 50mM Tartaric Acid pH=3.4 with NaOH
 Post Column PAR Detection at 520nm

Chromatogram of TMSTD



| Peak Name | Ret time | Area | Height | Type | Response | Amount |
|-----------|----------|---------|--------|------|-------------|---------|
| Cu | 4.71 | 1758708 | 183794 | BB | 1.75871e+06 | 0.5 ppm |
| Pb | 6.69 | 212112 | 15542 | BB | 2.12112e+05 | 1.0 |
| Zn | 12.27 | 1622314 | 73563 | BV | 1.62231e+06 | 0.5 |
| Ni | 13.66 | 1049294 | 38397 | VB | 1.04929e+06 | 1.0 |
| Co | 20.05 | 2543774 | 73778 | BB | 2.54377e+06 | 0.5 |
| Cd | 27.17 | 621232 | 13672 | BV | 6.21232e+05 | 1.0 |
| Fe | 28.36 | 451159 | 9671 | VB | 0.00000e+00 | |
| Mn | 37.55 | 3169191 | 53214 | BB | 3.16919e+06 | 1.0 |

Chromatogram of LP1TM



| Peak Name | Ret time | Area | Height | Type | Amount |
|-----------|----------|--------|--------|------|--------|
| UNKNOWN | 9.76 | 315111 | 37405 | BB | 0.000 |

Figure 5. Chromatogram of transition metals standard and transition metals in liquid propellant

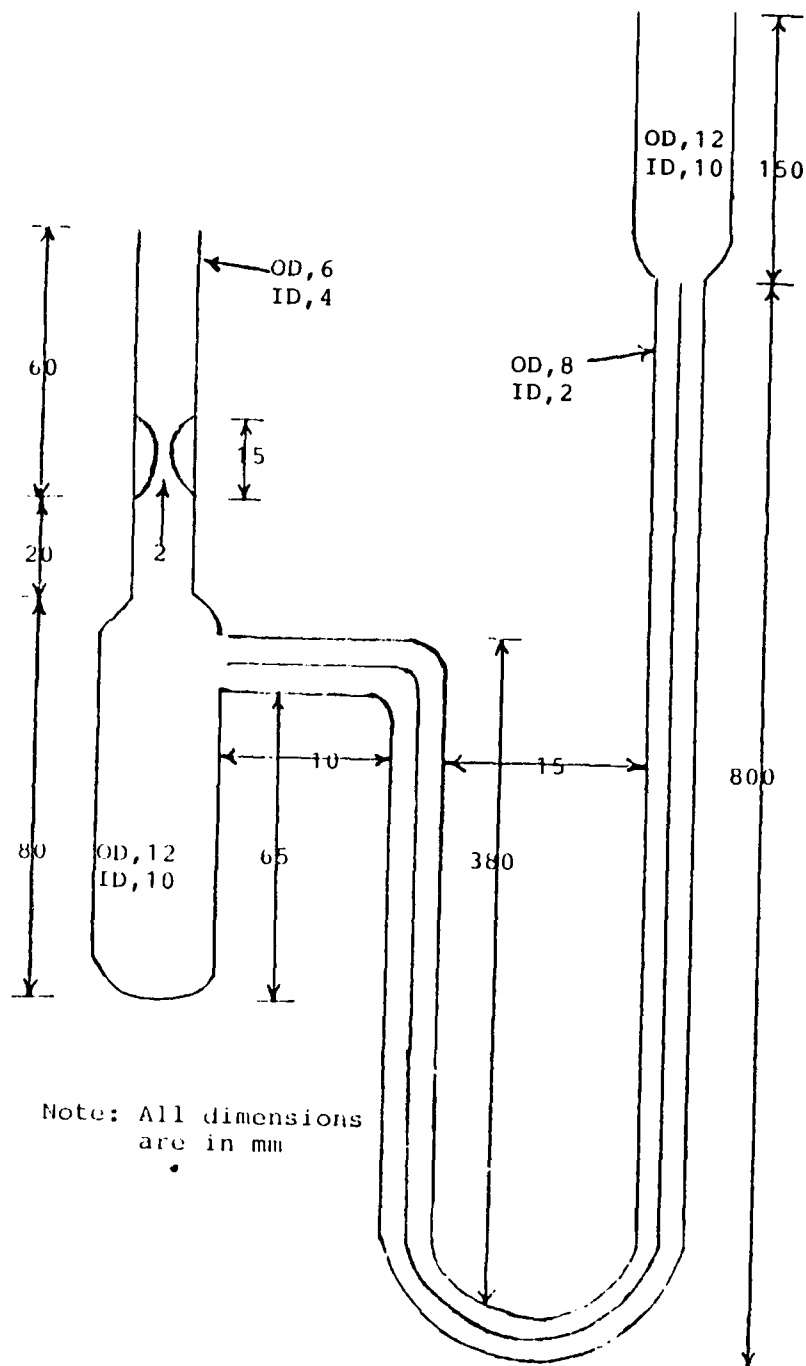


Figure 6. Pressure-time study apparatus

Vapor Pressure of LP1846 (LP-2) vs Temperature

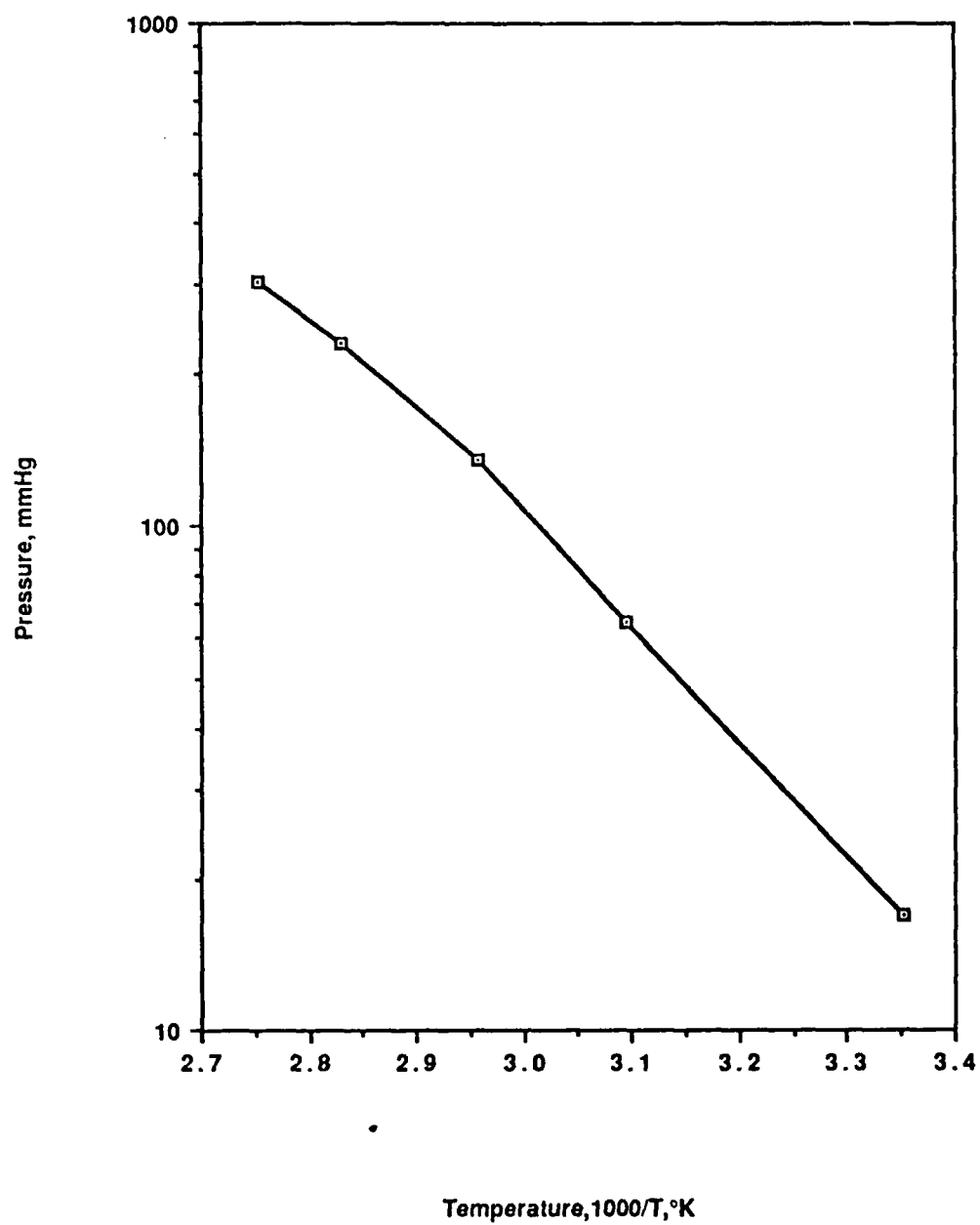


Figure 7. Vapor pressure of LP 1846

Density of LP1846 (LP-3) vs Temperature

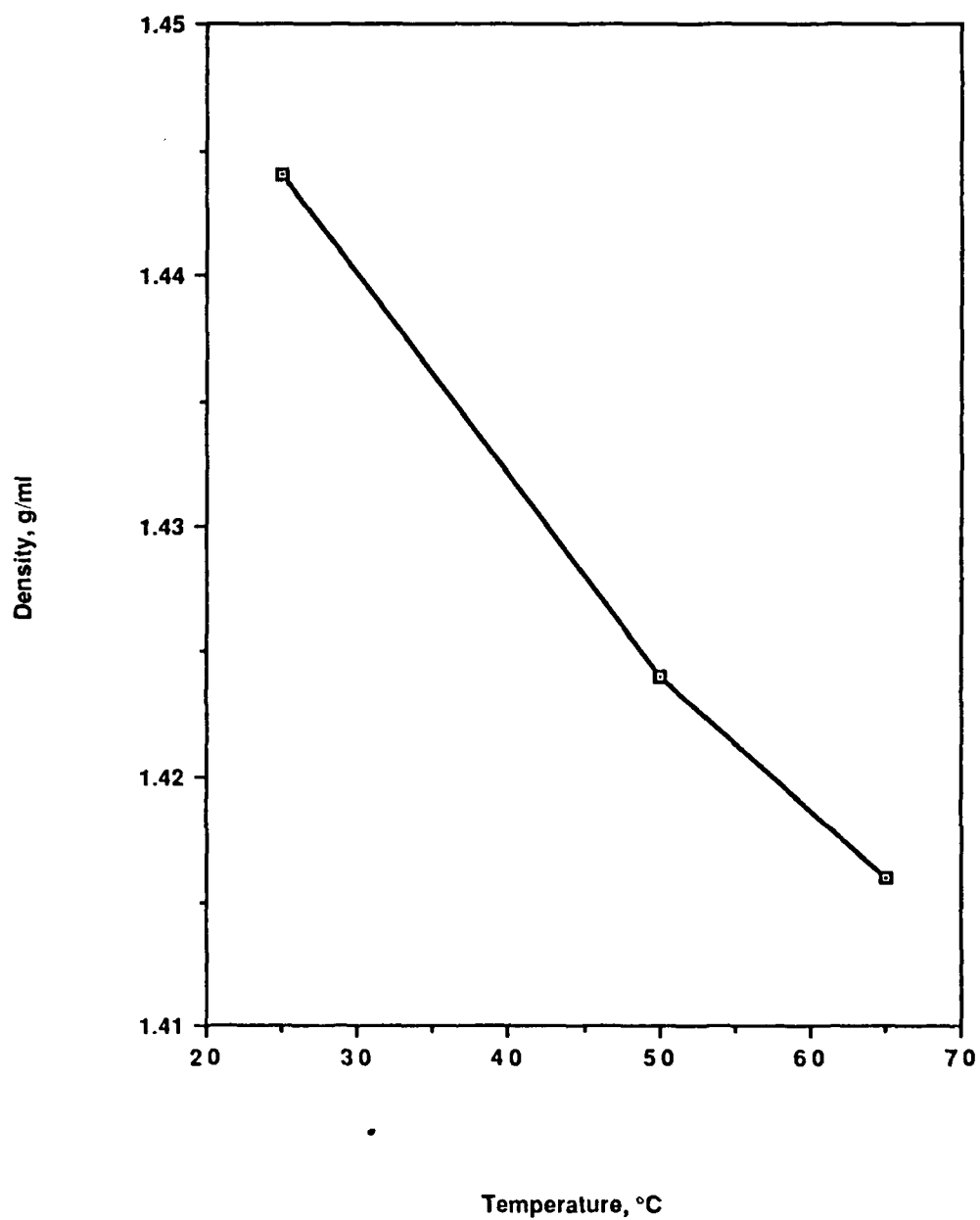
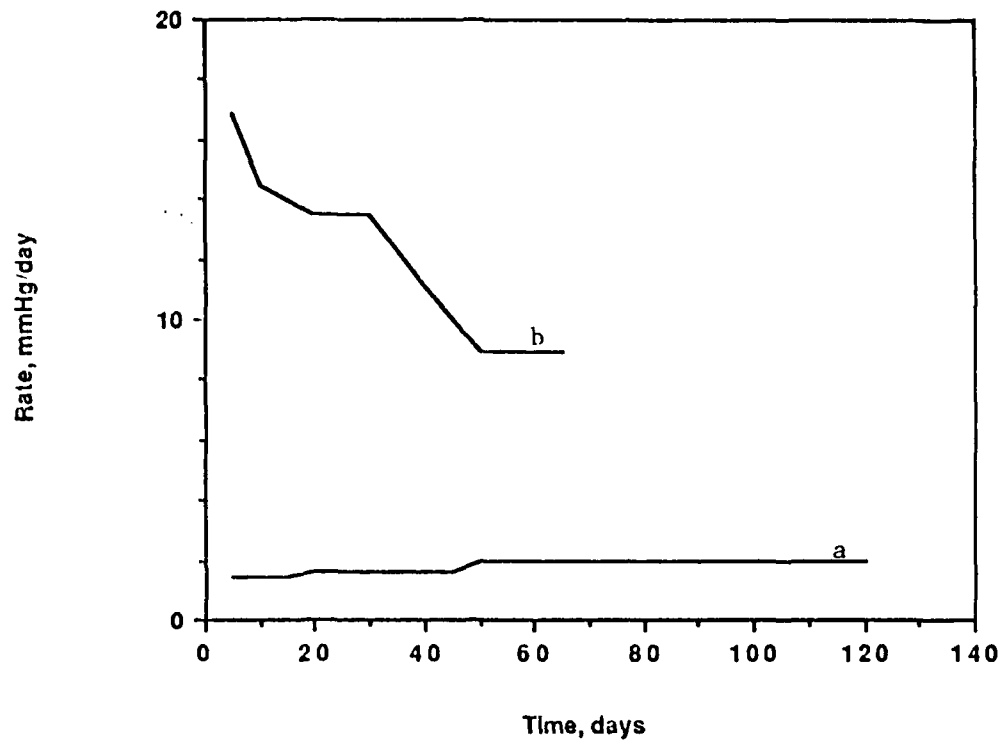


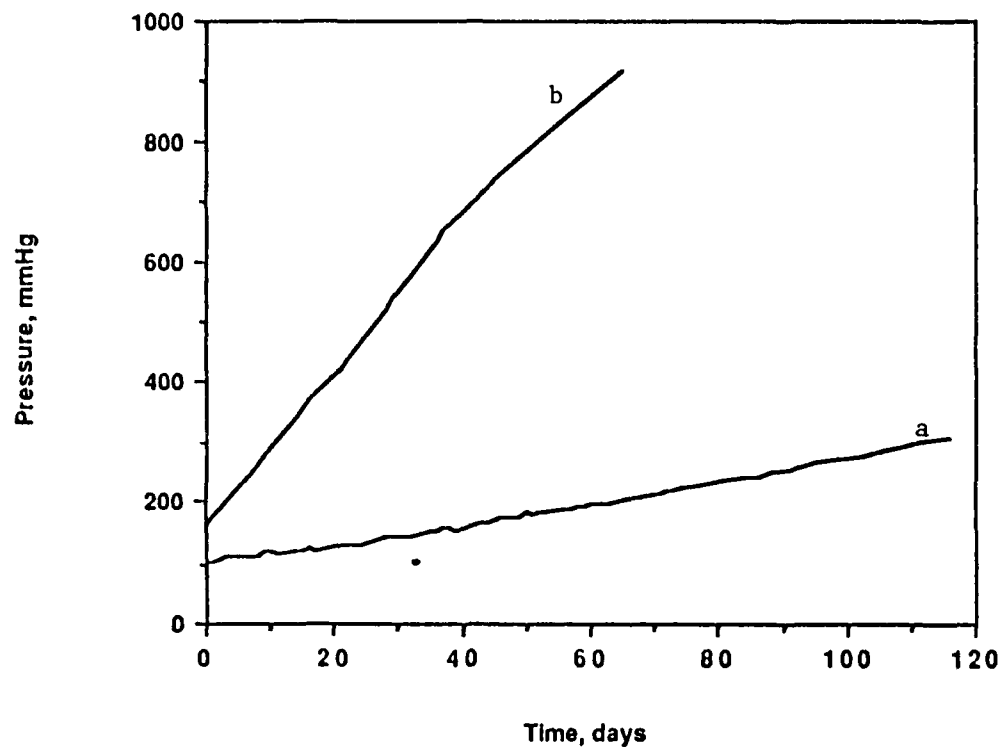
Figure 8. Density of LP 1846

Rate @ 50°C & 65°C - LP1846 (LP-2)



a 50C
b 65C

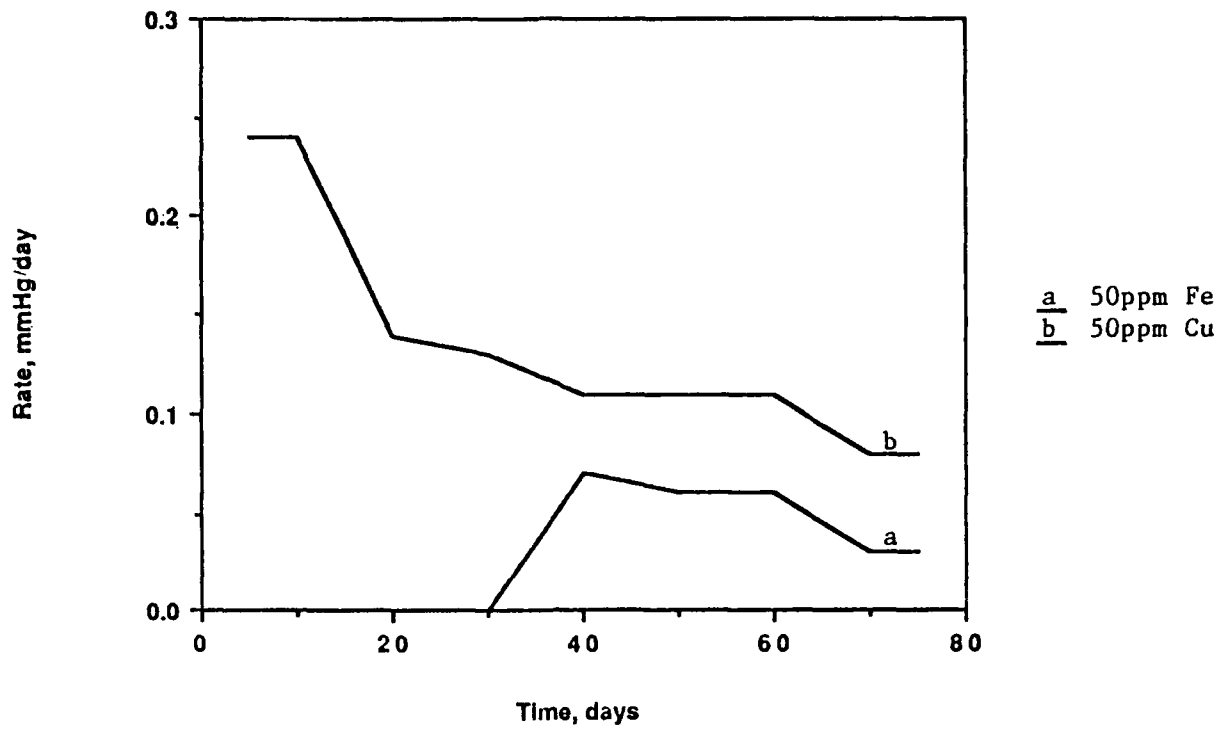
Pressure vs Time @ 50°C & 65°C - LP1846 (LP-2)



a 50°C
b 65°C

Figure 9. Pressure versus time and rate for LP 1846 containing 0.44% Nitric Acid at 50°C and 65°C

Rate @25°C - LP1846 (LP-3)



Pressure vs Time @25°C - LP1846 (LP-3)

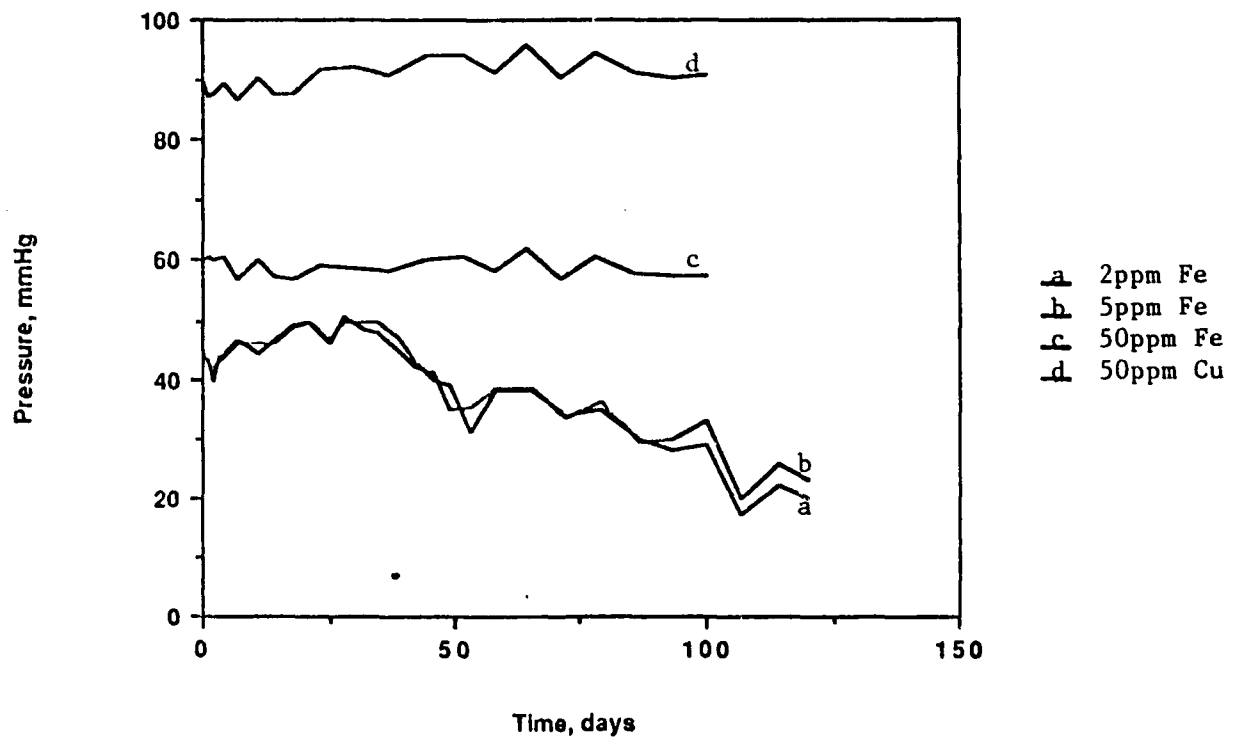
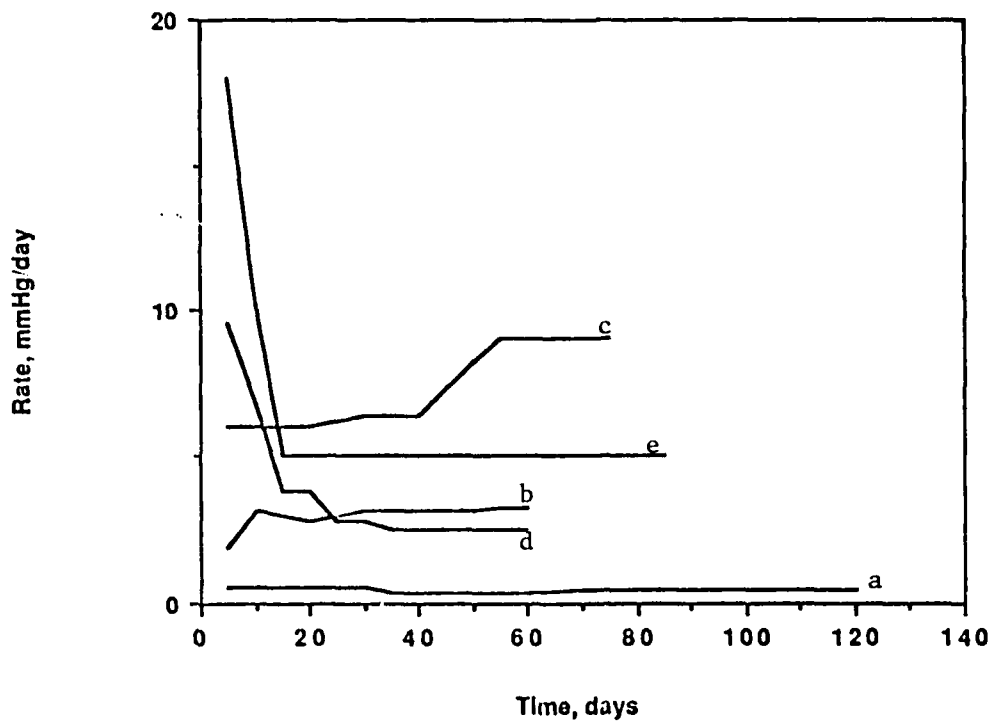


Figure 10. Pressure versus time and rate for LP 1846 containing iron and copper at 25°C

Rate @50°C - LP1846 (LP-3)



Pressure vs Time @50°C - LP1846 (LP-3)

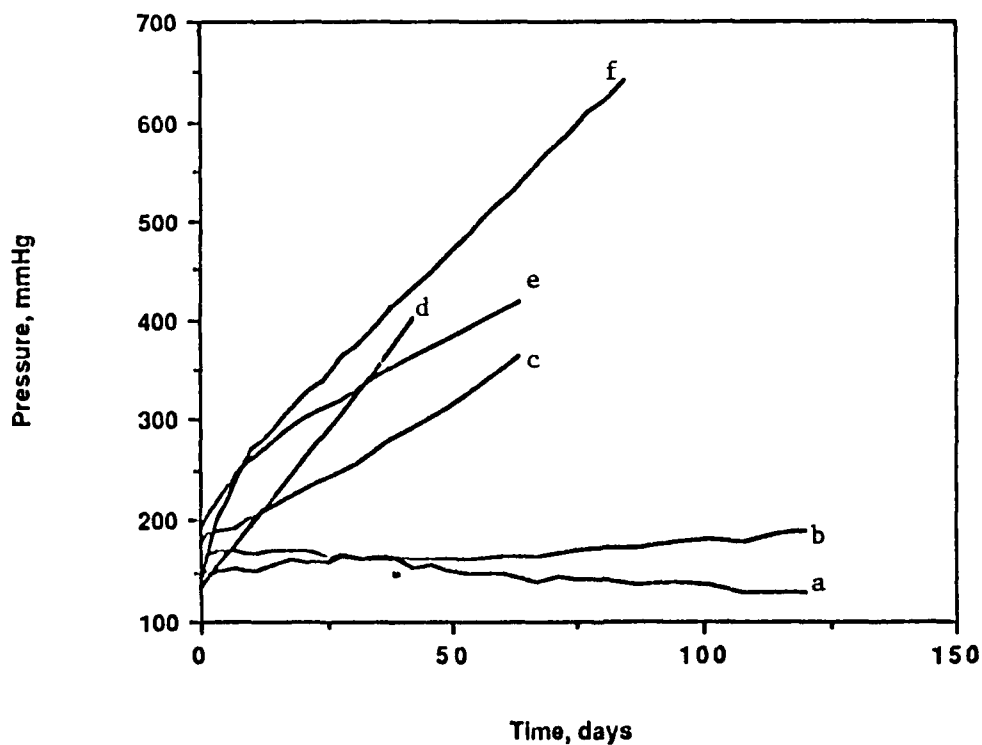
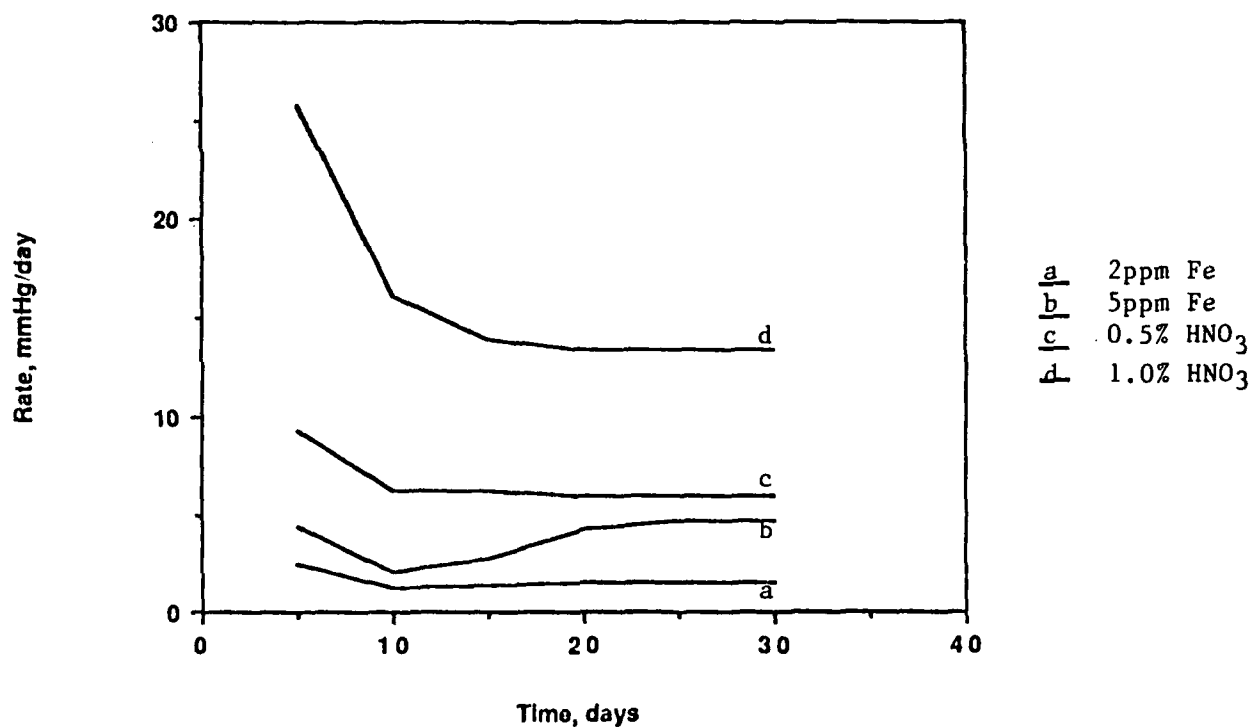


Figure 11. Pressure versus time and rate for LP 1846 containing iron and copper at 50°C

Rate @65°C - LP1846 (LP-3)



Pressure vs Time @65°C - LP1846 (LP-3)

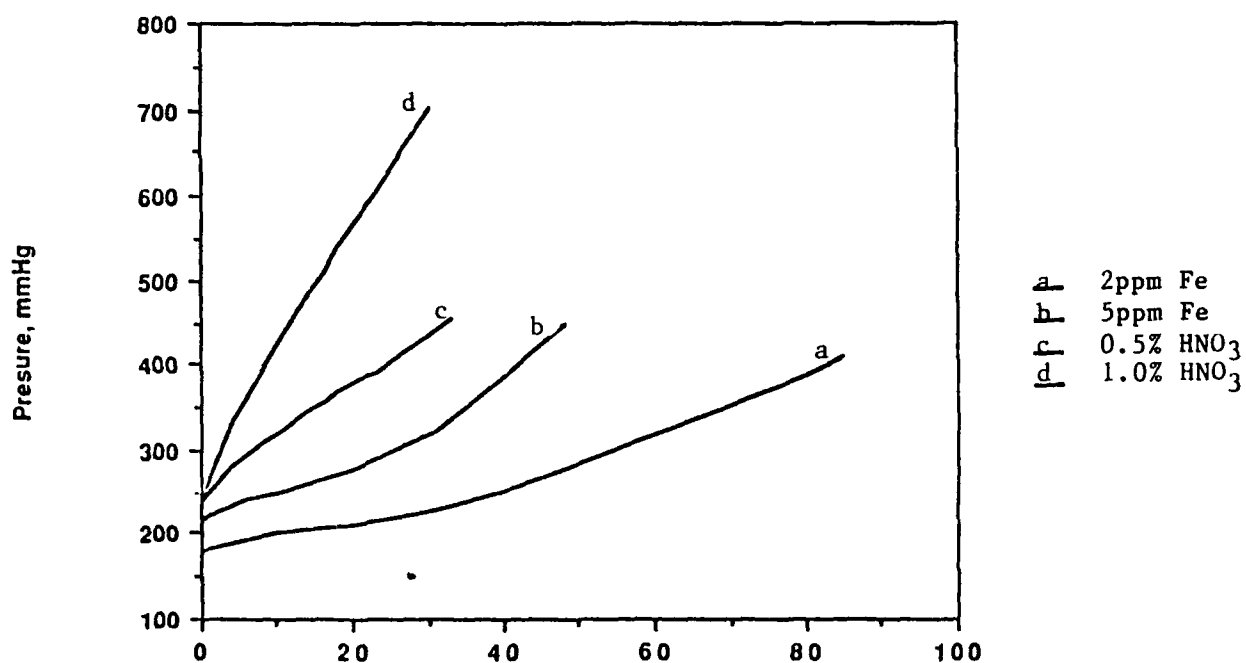


Figure 12. Pressure versus time and rate for LP 1846 containing iron and nitric acid at 65°C

REFERENCES

1. Seals, W.O., "Vulnerability Studies for a Liquid Propellant," Technical Report BRL-TR-2646, Ballistic Research Laboratory, Aberdeen Proving Ground, MD, 1984.
2. Decker, M.; Freeman, E.; Ward, J.; Tarantino, P.; and Davis, P., "Transition Metal Reactions in HAN-based Monopropellants," Proc. 22nd JANNAF Combustion Meeting, Vol I, p 177, CPIA Pub. 432, Chemical Propulsion Information Agency, Laurel MD, 1985.
3. Decker, M.; Klein, N.; Freedman, E.; "Titrimetric Analysis of Liquid Monopropellants," JANNAF Propellant Characterization Subcommittee Meeting, 1986.
4. Decker, M. and Freedman, E., "Analysis of Liquid Monopropellants by Titration." JANNAF 23rd Combustion Meeting, 1986.
5. Klein, N., "Liquid Propellant Stability Studies," Proc. 15th International ICT Conference on Technology of Propellants and High Explosives, 1984.
6. Research contribution by J. Krol, Waters Division of Millipore, 1988.

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